<Division of Synthetic Chemistry> Organoelement Chemistry

Division of Synthetic Chemistry
- Organoelement Chemistry -

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Visitors

Prof SCHAUMANN, Ernst — Technical University of Clausthal, Germany, 29–31 August 2006
Prof DEVILLANOVA, Francesco A — Departimento di Chimica Inorganica ed Analitica, Università degli Studi di Cagliari, Italy, 3–5 October 2006

Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivity between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts is also studied.

Research Activities (Year 2006)

Presentations

Application of Extremely Bulky Polythioether Ligands to the Synthesis of Novel Transition Metal Complexes Having a Unique Metallacyclic Framework, Tokitoh N, 11th International Symposium on Inorganic Ring Systems (IRIS XI), Oulu, Finland, 30 July– 4 August 2006 (Invited).

Design and Synthesis of Novel Polythioether Ligands Tethered with Extremely Bulky Substituents and Their Application to the Synthesis of Unique Transition Metal Complexes, Tokitoh N, 22nd International Symposium on the Organic Chemistry of Sulfur (ISOCS-22), Saitama, Japan, 20–25 August 2006 (Invited).

Grants

Tokitoh N, Takeda N, Sasamori T, Nagahora N, The Chemistry of Unsaturated Compounds of Heavier Main Group Elements: Pursuit of Novel Properties and Functions, Grant-in-Aid for Creative Scientific Research, 1 April 2005–31 March 2009.

Tokitoh N, Synthesis of Dynamic Complexes Contain-

Synthesis of the Stable "Heavier Alkyne"

Triple-bond compounds between heavier group 14 elements, which are called "*dimetallynes*", are one of the most fascinating classes of compounds in organometallic chemistry. The chemistry of dimetallynes has been developed in these several years and the syntheses of all symmetrical combinations (Si≡Si, Ge≡Ge, Sn≡Sn, Pb≡Pb) have been achieved by taking advantage of kinetic stabilization using bulky substituents. However, the stable examples of dimetallynes are too limited to elucidate their properties sufficiently. We have succeeded in the synthesis of a new example of a stable germanium analogue, *digermyne* **1**, by using an efficient steric protection group, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt), and revealed its properties. The reaction of dibromodigermene **2** with KC_8 in benzene resulted in the formation of digermyne **1**. The triple-bond character of **1** was fully examined based on the results of spectroscopic and X-ray crystallographic analyses, and theoretical calculations together with studies on the reactivities. Digermyne **1** showed a shorter Ge≡Ge bond length than that of the previously reported digermyne, ArGe≡GeAr (Ar = 2,6-[(*i*-Pr)$_2$C$_6$H$_3$]$_2$-C$_6$H$_3$-).

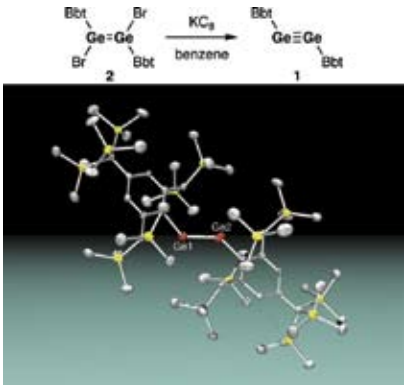

Figure 1. Synthesis of the stable digermyne, **1**, and its structure.

Synthesis and Applications of a New β-Diketiminato Ligand

The chemistry of β-diketiminato ligands has been extensively studied, and it has been revealed that they can stabilize the metals with unusual valency, such as group 4 metals. In this project, we have studied the synthesis of a new lithium β-diketiminato **3** bearing an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, and its application toward complexation with group 4 metals. Reactions of **3** with [$MCl_4(thf)_2$] (M = Ti, Zr, Hf) gave the corresponding trichlorides **4a-c**. The structures of **4a-c** were definitively determined by X-ray crystallographic analysis. Next, with expectation of obtaining the corresponding low-valent compounds of group 4 metals, the reductions of **4a-c** were attempted. The reactions of **4a-c** with KC_8 in the presence of TMEDA and LiCl resulted in the formation of unexpected imido complexes **5a-c**, respectively.

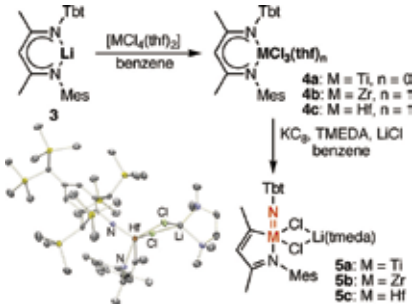

Figure 2. Syntheses of the complexes **4** and **5** and structure of the Hf complex **5c**.

ing Heteroatoms by Taking Advantage of Kinetic Stabilization, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2002–31 March 2006.

Sasamori T, Synthesis of Novel π Electron Conjugated Systems Containing Heavier Group 14 and 15 Elements and the Elucidation of Their Properties, Grant-in-Aid for Young Scientists (B), 1 April 2004–31 March 2006.

Sasamori T, Synthesis of Novel Molecular Wire with π Electron Systems Containing Silicon and Phosphorus, Kinki Invention Center, 1 April 2005–31 March 2006.

Mizuhata Y, Synthesis, Structure, and Properties of Kinetically Stabilized Tin-carbon Double-bond Compounds, Grant-in-Aid for JSPS Fellows, 1 April 2005–31 March 2006.

Sasamori T, Construction of Novel Extended π-Electron Conjugated Systems Containing Heavier Main Group Elements, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Awards

Nagahora N, The Best Oral Presentation Award, The 86th Annual Meeting of the Chemical Society of Japan, May 2006.

Mizuhata Y, The Student Lecture Award, The 86th Annual Meeting of the Chemical Society of Japan, May 2006.

Matsumoto T, The Best Poster Award, 18th Symposium on Fundamental Organic Chemistry, Japan, 9 October 2006.

Nakamura K, Yamanaka R, Matsuda T, Harada T, Tetrahedron: Asymmetry Most Cited Paper 2003–2006 Award, October 2006.

Takeda N, The Society of Synthetic Organic Chemistry, Japan, Kansai Branch Awards, 8 November 2006.

Sasamori T, The ICR Award for Young Scientists, 15 December 2006.